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October 25, 2004

**By fax: 011.49.89.2399.4465**
**Confirmation by messenger**

European Patent Office
PCT Division
Attention: T. Jenn, Authorized Officer
Erhardtstraße 27
D-80331 Münich
GERMANY

**RESPONSE TO WRITTEN OPINION**

Re: A PROCESS AND AN APPARATUS FOR PRODUCING CALCIUM CARBONATE VIA AN ENZYMATIC PATHWAY
International Patent Application No. PCT/CA03/01070
Inventors: Frédérick ANCTIL et al.
O/Ref. 000677-0032

Madam:
Sir:

In response to the written opinion dated June 24, 2004, for which the time limit for replying to has been extended until October 24, 2004, please amend the above-identified patent application as follows.

**IN THE DESCRIPTION:**

Please cancel pages 1 to 4 presently on file and substitute therefor the new corresponding pages enclosed herewith.

**IN THE CLAIMS:**

Please cancel the set of 14 claims presently on file and substitute therefor the new corresponding set of 11 claims enclosed herewith.

**REMARKS**

In order to facilitate the examination of the amended application, you will find enclosed a copy of the handwritten amendments carried out in the description and the claims.

**MODIFICATIONS TO THE DESCRIPTION**

The "Background of the invention", on page 1, has been amended to detail equation [1], which is the result of equations [1a] to [1e] added to the description.

The same equations have been added to page 4 to better explain the reactions occurring in the process for producing $CaCO_3$ according to the invention.

Also in the description of the "Background of the invention", on page 2, a description of WO9855210 in the name of the Applicant has been added.

Page 2 of the description has been further amended to bring the statement of the inventive idea of the invention in conformity with new claim 1, as required by rule 5.1(a)(iii) PCT.

**MODIFICATIONS TO THE CLAIMS**

In order to better define the invention over the prior art cited by the Examiner, a new claim 1 is proposed which is a combination of former claims 1, 2 and 3.

Former claim 9 (new claim 7) has also been amended to include therein the subject matter of former claims 10 and 11.

A new claim 11 has been added to better cover a further aspect of the invention.

Accordingly, claims 2, 3, 10 and 11 have been deleted and the remaining claims have been renumbered.

More specifically, new claims 2 to 6 correspond respectively to former claims 4 to 8 and new claims 8 to 10 correspond to former claims 12 to 14, respectively.

The Applicant has noted the statement that original claims 2, 3, 10 and 11 lack inventiveness, in combining D1, D2 and D3 cited by the Examiner. It is however believed that new claim 1, which is a combination of former claims 1 to 3, and new claim 7, which is a combination of former claims 9 to 11, are patentably distinguishable from the prior art cited by the Examiner. More specifically, it is submitted that even though an ordinary person skilled in the art would look at documents D1, D2 and D3, he would not easily be able to combine the features coming from a mosaic of those documents to obtain the matter of independent claims 1 and 7. To do so, that person would have to use inventive skill. Thus, the subject matter of new claims 1 and 7 does involve an inventive step, and thus, satisfies the criterion set forth in article 33(3) PCT.

For these reasons, the new set of claims is believed to meet the requirements of novelty and inventiveness, and the Examiner is thus respectfully requested to reach a favourable statement of novelty and inventiveness in this case.

Yours very truly,

ROBIC g.p.

Nathalie Jodoin, Eng.
Lawyer and Patent Agent

NJ/lm

Encl. - amended pages 1, 2, 3, 4, 4a and pages of claims 1 to 11
- copy of pages with handwritten amendments

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# A PROCESS AND AN APPARATUS FOR PRODUCING CALCIUM CARBONATE VIA AN ENZYMATIC PATHWAY

## FIELD OF THE INVENTION

The present invention generally relates to the field of calcium carbonate production obtained by precipitation. More particularly, it concerns a process for preparing precipitated calcium carbonate (hereinafter referred to as PCC) involving the use of an enzyme that directly supplies a source of bicarbonate ions which are required by the PCC production process. The present invention is particularly useful in the pulp and paper industry.

## BACKGROUND OF THE INVENTION

Production of $CaCO_3$

Calcium carbonate is used in different fields, most importantly in the pulp and paper industry, where it is largely used for coating the paper after it has been pressed, thereby increasing the printing quality of the paper, as well as its color, smoothness, and strength.

The traditional process of forming solid $CaCO_3$ consists in bubbling carbon dioxide in milk of lime ($Ca(OH)_2$). This process allows a sufficient amount of $CO_2$ to solubilize and produce solid calcium carbonate according to the following equation:

$$Ca(OH)_2 + CO_2 \longleftrightarrow CaCO_3 + H_2O \qquad [1]$$

Reaction (1) is the result of the following reactions:

$$CO_2 + H_20 \longleftrightarrow H^+ + HCO_3^- \qquad [1a]$$

$$HCO_3^- \longleftrightarrow H^+ + CO_3^{-2} \qquad [1b]$$

$$Ca\,(OH)_2 \longleftrightarrow Ca^{2+} + 2\,OH^- \qquad [1c]$$

$$Ca^{2+} + CO_3^{-2} \longleftrightarrow CaCO_3 \qquad [1d]$$

$$2\,OH^- + 2\,H^+ \longleftrightarrow 2\,H_2O \qquad [1e]$$

This reaction (1) is a rather slow reaction and one drawback thus encountered with the same is its low production yield as compared to the need of $CaCO_3$ in the pulp and paper industry or in other fields.

There is thus presently a need for a process for the production of $CaCO_3$ that provides a better production yield.

Conversion of $CO_2$ into hydrogen ions and bicarbonate ions

EP0991462; AU7753398; WO9855210; CA2291785 in the name of the Applicant disclose the use of the enzyme carbonic anhydrase to catalyse the hydration of $CO_2$ into hydrogen ions and bicarbonate ions. The reaction that allows for the production of bicarbonate in the presence of the enzyme is represented by equation [2]:

$$CO_2 + H_2O \overset{\text{enzyme}}{\longleftrightarrow} H^+ + HCO_3^- \qquad [2]$$

The hydration kinetics of $CO_2$, with or without enzyme, has been the object of several scientific works. The reaction rate constant of non-catalysed (without enzyme) reactions is in the order of $0{,}035 s^{-1}$ (25°C, pH=7)[1]. At an elevated pH (pH > 10), the hydroxyl ions ($OH^-$) contribute to the catalysis, and consequently, the reaction rate constant can attain $8.5 \times 10^3\ s^{-1}$ at 25°C[2]. The catalysed reaction (with enzyme), can also be associated with an elevated reaction rate constant in the order of $1{,}4 \times 10^6$ (25°C, pH= 8.8)[3]. The ratio of the two reaction rate constants allows one to predict the $CO_2$ hydration kinetics, which can be in the order of 50 million times more elevated when an enzyme is present and depending on the experimental conditions.

WO9855210 in the name of the Applicant also discloses the possibility to recycle the liquid phase used for $CO_2$ absorption given bicarbonate ions and protons are removed by an auxiliary unit.

## SUMMARY OF THE INVENTION

An object of the present invention is to provide a process and an apparatus for the production of $CaCO_3$ that satisfies the above-mentioned need for a process that provides an increased production yield of precipitated calcium carbonate (PCC).

In accordance with the present invention, that object is achieved with a process for producing $CaCO_3$, charaterized in that it comprises the steps of:

a) catalysing the hydration of $CO_2$ contained in a $CO_2$-containing gas by means of an enzyme capable of catalysing the hydration of dissolved $CO_2$ into hydrogen ions and bicarbonate ions, thereby producing a solution containing bicarbonate ions and hydrogen ions, said enzyme being carbonic anhydrase;

b) reacting the bicarbonate ions contained in the solution obtained in step a) with calcium ions, thereby producing a solution containing $CaCO_3$;

c) precipitating the $CaCO_3$ contained in the solution obtained in step b); and

wherein the step b) comprises the step of:

– mixing the solution obtained in step a) with $Ca(OH)_2$, thereby providing simultaneously said calcium ions for $CaCO_3$ production and $OH^-$ ions for $H^+$ neutralisation.

The $CaCO_3$ is thus produced from milk of lime ($Ca(OH)_2$) and $CO_2$ as in the prior art, although it shows an improved yield, as explained hereinafter.

As mentioned above, the traditional process of forming $CaCO_3$ consists in bubbling carbon dioxide in milk of lime ($Ca(OH)_2$). This process produces solid calcium carbonate according to the following equation:

$$Ca(OH)_2 + CO_2 \longleftrightarrow CaCO_3 + H_2O \qquad [1]$$

This non catalyzed solubilization of gaseous $CO_2$ in an aqueous medium implies the following series of natural reversible reactions. The equilibrium constants of these natural reactions are well known in the prior art.

$$CO_2 + H_2O \longleftrightarrow H_2CO_3 \quad K \cong 600 \text{ à } 25°C \quad (K \equiv [CO_2]/[H_2CO_3]) \quad [3]$$

$$H_2CO_3 \longleftrightarrow H^+ + HCO_3^- \quad K = 4{,}47 \times 10^{-7} \text{ à } 25°C \quad (K= [HCO_3^-][H^+]/[H_2CO_3]) \quad [4]$$

$$HCO_3^- \longleftrightarrow H^+ + CO_3^{2-} \quad K = 4{,}70 \times 10^{-11} \text{ à } 25°C \quad (K= [CO_3^{2-}][H^+]/[HCO_3^-]) \quad [5]$$

From a thermodynamic point of view, the large equilibrium constant associated to equation [3] translates into a weak inherent tendency to produce the acid ($K_{eq} = [CO_2]/[H_2CO_3] \cong 600$) (<u>Chemistry of the Elements</u> (2nd edition, Butterworth Heinemann, p. 310 (1997)).

Equation [3], representing the formation of carbonic acid ($H_2CO_3$), is in reality the limiting step of the process for producing bicarbonate.

Thus, the use of an enzyme, preferably carbonic anhydrase, which is specific to $CO_2$ molecules, avoids the step of carbonic acid formation. In other words, the enzyme catalyses the hydration of $CO_2$ by eliminating the limiting step of the process. As mentioned above, the reaction that allows for the production of bicarbonate in the presence of the enzyme is represented by equation [2]:

$$CO_2 + H_2O \overset{\text{enzyme}}{\longleftrightarrow} H^+ + HCO_3^- \quad [2]$$

Reaction [2] allows for the production of an aqueous solution having a high $HCO_3^-$ ion content that is used in the process of producing PPC. This concept is represented in the following equation:

$$HCO_3^- + H^+ + Ca(OH)_2 \longleftrightarrow CaCO_3 + 2\, H_2O \quad [6]$$

Equation 6 is the result of the following equations:

$$HCO_3^- \longleftrightarrow H^+ + CO_3^{-2} \quad [1b]$$

$$Ca\,(OH)_2 \longleftrightarrow Ca^{2+} + 2\, OH^- \quad [1c]$$

$Ca^{2+} + CO_3^{-2}$ <--------> $CaCO_3$ [1d]

$2\ OH^- + 2\ H^+$ <--------> $2\ H_2O$ [1e]

From equations [1] and [6], one can see that the reaction for producing PCC performs better in the presence of an enzymatic bioreactor supplied with gaseous $CO_2$ which in turn directly supplies $HCO_3^-$ to the process for preparing precipitated calcium carbonate. The improvement resides not only in the increased hydration rate of $CO_2$, but also in the increased amounts of $CaCO_3$ formed in a given reaction time. The variation of Gibbs free energy ($\Delta G$) for each of the reactions will indeed allow one to determine which of the two chemical reactions is favourable from a thermodynamic point of view.

Reaction [6], having a $\Delta G$ in the order of -119 kJ/mol, is more favourable from a thermodynamic point of view than reaction [1] which has a $\Delta G$ value in the order of -74 kJ/mol. The respective equilibrium constant of these two chemical reactions is calculated using equation [7]:

$$-\Delta G = RT \ln(K_{eq}) \qquad [7]$$

The equilibrium constant of a chemical reaction not containing enzyme is about $9{,}36 \times 10^{12}$ at 298K, while a catalysed reaction making use of an enzyme is about $7{,}24 \times 10^{20}$. While the equilibrium constant is higher for a reaction containing an

**CLAIMS**

1. A process for producing $CaCO_3$, characterized in that it comprises the steps of:

a) catalysing the hydration of $CO_2$ contained in a $CO_2$-containing gas by means of an enzyme capable of catalysing the hydration of dissolved $CO_2$ into hydrogen ions and bicarbonate ions, thereby producing a solution containing bicarbonate ions and hydrogen ions, said enzyme being carbonic anhydrase;

b) reacting the bicarbonate ions contained in the solution obtained in step a) with calcium ions, thereby producing a solution containing $CaCO_3$;

c) precipitating the $CaCO_3$ contained in the solution obtained in step b); and

wherein the step b) comprises the step of:

– mixing the solution obtained in step a) with $Ca(OH)_2$, thereby providing simultaneously said calcium ions, for $CaCO_3$ production and $OH^-$ ions for $H^+$ neutralisation.

2. A process according to claim 1, characterized in that step a) of hydration of $CO_2$ is performed in a bioreactor comprising a reaction chamber filled with said enzyme and the step b) is performed in at least one separate reaction tank, the process further comprising a step of directing a flow of said solution from said bioreactor into said reaction tank.

3. A process according to claim 2, characterized in that the reaction chamber is filled with packing on which the enzyme is immobilized.

4. A process according to any one of claims 1 to 3, characterized in that step b) is performed under stirring to prevent the calcium carbonate from settling.

5. A process according to any one of claims 1 to 4, characterized in that it comprises an additional step of:

d) separating the precipitate of $CaCO_3$ of step c) from the solution.

6. A process according to claim 7, characterized in that step d) of separating consists of filtering.

7. An apparatus for producing $CaCO_3$ according to the process defined in claim 1, characterized in that it comprises:

– catalyzing means for catalysing the hydration of the $CO_2$ into bicarbonate ions and hydrogen ions;

– reacting means for reacting the bicarbonate ions and protons obtained in the catalyzing means with calcium ions and hydroxyl ions to produce $CaCO_3$; and

– precipitating means for precipitating the $CaCO_3$ obtained in the reacting means; wherein

the means for catalyzing the hydration of the $CO_2$ comprises a bioreactor comprising:

– a gas inlet for receiving gaseous $CO_2$;

– a liquid inlet for receiving an aqueous liquid;

– a reaction chamber in fluid communication with the gas inlet and the liquid inlet, the reaction chamber containing therein carbonic anhydrase for catalysing the hydration of dissolved $CO_2$ into bicarbonate ions and hydrogen ions; and

- a liquid outlet in fluid communication with the reaction chamber for discharging a solution of bicarbonate ions and hydrogen ions.

8. An apparatus as claimed in claim 7, characterized in that the means for reacting the bicarbonate ions with calcium ions and precipitating $CaCO_3$ is at least

one reaction tank having an inlet in fluid communication with the liquid outlet of the bioreactor and an outlet to discharge a solution containing $CaCO_3$.

9. An apparatus as claimed in claim 11, characterized in that it comprises a buffer tank having an inlet in fluid communication with the outlet of the at least one reaction tank for receiving and reserving the solution obtained in said at least one reaction tank for a further treatment.

10. An apparatus according to claim 9, characterized in that it comprises a filter in fluid communication with said buffer tank to separate the $CaCO_3$ from the solution.

11. An apparatus according to claim 10, characterized in that the solution free of $CaCO_3$ is recycled and reused in the reaction tank.

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This reaction (1) is a rather slow reaction and one drawback thus encountered with the same is its low production yield as compared to the need of $CaCO_3$ in the pulp and paper industry or in other fields.

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WO9855210 in the name of the Applicant also discloses the possibility to recycle the liquid phase used for $CO_2$ absorption given bicarbonate ions and protons are removed by an auxiliary unit.

## SUMMARY OF THE INVENTION

An object of the present invention is to provide a process and an apparatus for the production of $CaCO_3$ that satisfies the above-mentioned need for a process that provides an increased production yield of precipitated calcium carbonate (PCC).

In accordance with the present invention, that object is achieved with a process for producing $CaCO_3$, charaterized in that it comprises the steps of:

a) catalysing the hydration of $CO_2$ contained in a $CO_2$-containing gas by means of an enzyme capable of catalysing the hydration of dissolved $CO_2$ into hydrogen ions and bicarbonate ions, thereby producing a solution containing bicarbonate ions and hydrogen ions;

b) reacting the bicarbonate ions contained in the solution obtained in step a) with calcium ions, thereby producing a solution containing $CaCO_3$; and

c) precipitating the $CaCO_3$ contained in the solution obtained in step b).

The enzyme used in the process is preferably carbonic anhydrase or an analogue thereof.

In accordance with a preferred aspect, step b) comprises the step of mixing the solution obtained in step a) with $Ca(OH)_2$, thereby providing the calcium ions. In that case, the $CaCO_3$ is thus produced from milk of lime ($Ca(OH)_2$) and $CO_2$ as in the prior art, although it shows an improved yield, as explained hereinafter.

As mentioned above, the traditional process of forming $CaCO_3$ consists in bubbling carbon dioxide in milk of lime ($Ca(OH)_2$). This process produces solid calcium carbonate according to the following equation:

$$Ca(OH)_2 + CO_2 \longleftrightarrow CaCO_3 + H_2O \qquad [1]$$

This non catalyzed solubilization of gaseous $CO_2$ in an aqueous medium implies the following series of natural reversible reactions. The equilibrium constants of these natural reactions are well known in the prior art.

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$$H_2CO_3 \longleftrightarrow H^+ + HCO_3^- \quad K = 4{,}47 \times 10^{-7} \text{ à } 25°C \quad (K= [HCO_3^-][H^+]/[H_2CO_3]) \quad [4]$$

$$HCO_3^- \longleftrightarrow H^+ + CO_3^{2-} \quad K = 4{,}70 \times 10^{-11} \text{ à } 25°C \quad (K= [CO_3^{2-}][H^+]/[HCO_3^-]) \quad [5]$$

From a thermodynamic point of view, the large equilibrium constant associated to equation [3] translates into a weak inherent tendency to produce the acid ($K_{eq} = [CO_2]/[H_2CO_3] \cong 600$) (<u>Chemistry of the Elements</u> (2nd edition, Butterworth Heinemann, p. 310 (1997)).

Equation [3], representing the formation of carbonic acid ($H_2CO_3$), is in reality the limiting step of the process for producing bicarbonate.

Thus, the use of an enzyme, preferably carbonic anhydrase, which is specific to $CO_2$ molecules, avoids the step of carbonic acid formation. In other words, the enzyme catalyses the hydration of $CO_2$ by eliminating the limiting step of the process. As mentioned above, the reaction that allows for the production of bicarbonate in the presence of the enzyme is represented by equation [2]:

$$CO_2 + H_2O \overset{\text{enzyme}}{\longleftrightarrow} H^+ + HCO_3^- \quad [2]$$

Reaction [2] allows for the production of an aqueous solution having a high $HCO_3^-$ ion content that is used in the process of producing PPC. This concept is represented in the following equation:

$$HCO_3^- + H^+ + Ca(OH)_2 \longleftrightarrow CaCO_3 + 2\,H_2O \quad [6]$$

<u>Equation 6 is the result of the following equations:</u>

$$HCO_3^- \longleftrightarrow H^+ + CO_3^{-2} \quad [1b]$$

$$Ca(OH)_2 \longleftrightarrow Ca^{2+} + 2\,OH^- \quad [1c]$$

$$Ca^{2+} + CO_3^{-2} \longleftrightarrow CaCO_3 \quad [1d]$$

$$2\,OH^- + 2\,H^+ \longleftrightarrow 2\,H_2O \quad [1e]$$

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**CLAIMS**

1. A process for producing $CaCO_3$, characterized in that it comprises the steps of:

a) catalysing the hydration of $CO_2$ contained in a $CO_2$-containing gas by means of an enzyme capable of catalysing the hydration of dissolved $CO_2$ into hydrogen ions and bicarbonate ions, thereby producing a solution containing bicarbonate ions and hydrogen ions~~;~~, said enzyme being carbonic anhydrase;

b) reacting the bicarbonate ions contained in the solution obtained in step a) with calcium ions, thereby producing a solution containing $CaCO_3$; and

c) precipitating the $CaCO_3$ contained in the solution obtained in step b)~~.~~; and

wherein ~~2. A process according to claim 1, characterized in that~~ step b) comprises the step of: simultaneously

-mixing the solution obtained in step a) with $Ca(OH)_2$, thereby providing said calcium ions~~.~~ for $CaCO_3$ production and $OH^-$ ions for $H^+$ neutralisation

~~3. A process according to claim 1 or 2, characterized in that said enzyme is carbonic anhydrase or an analogue thereof.~~

2 ~~4.~~ A process according to any ~~one of~~ claims 1 ~~to 3~~, characterized in that step a) of hydration of $CO_2$ is performed in a bioreactor comprising a reaction chamber filled with said enzyme and the step b) is performed in at least one separate reaction tank, the process further comprising a step of directing a flow of said solution from said bioreactor into said reaction tank.

3 ~~5.~~ A process according to claim ~~4~~ 2, characterized in that the reaction chamber is filled with packing on which the enzyme is immobilized.

4 ~~6.~~ A process according to any one of claims 1 to ~~5~~ 3, characterized in that step b) is performed under stirring to prevent the calcium carbonate from settling.

~~7~~ 5. A process according to any one of claims 1 to ~~6~~ 4, characterized in that it comprises an additional step of:

d) separating the precipitate of $CaCO_3$ of step c) from the solution.

~~8~~ 6. A process according to claim ~~6~~ 7, characterized in that step d) of separating consists of filtering.

~~9~~ 7. An apparatus for producing $CaCO_3$ according to the process defined in claim 1, characterized in that it comprises:

- catalyzing means for catalysing the hydration of the $CO_2$ into bicarbonate ions and hydrogen ions;

-reacting means for reacting the bicarbonate ions and protons obtained in the catalyzing means with calcium ions and hydroxyl ions to produce $CaCO_3$; and

-precipitating means for precipitating the $CaCO_3$ obtained in the reacting means; wherein

~~10. An apparatus according to claim 9, characterized in that~~ the means for catalyzing the hydration of the $CO_2$ comprises a bioreactor comprising:

-a gas inlet for receiving gaseous $CO_2$;

-a liquid inlet for receiving an aqueous liquid;

-a reaction chamber in fluid communication with the gas inlet and the liquid inlet, the reaction chamber containing therein carbonic anhydrase for ~~enzymes capable of~~ catalysing the hydration of dissolved $CO_2$ into bicarbonate ions and hydrogen ions; and

- a liquid outlet in fluid communication with the reaction chamber for discharging a solution of bicarbonate ions and hydrogen ions.

~~11. An apparatus as claimed in claim 10, characterized in that the enzyme is carbonic anhydrase.~~

8 ~~12~~. An apparatus as claimed in claim 7 ~~10 or 11~~, characterized in that the means for reacting the bicarbonate ions with calcium ions and precipitating $CaCO_3$ is at least one reaction tank having an inlet in fluid communication with the liquid outlet of the bioreactor and an outlet to discharge a solution containing $CaCO_3$.

9 ~~13~~. An apparatus as claimed in claim 8 ~~12~~, characterized in that it comprises a buffer tank having an inlet in fluid communication with the outlet of the at least one reaction tank for receiving and reserving the solution obtained in said at least one reaction tank for a further treatment.

10 ~~14~~. An apparatus according to claim 9 ~~13~~, characterized in that it comprises a filter in fluid communication with said buffer tank to separate the $CaCO_3$ from the solution.

11. An apparatus according to claim 10, characterised in that the solution free ~~of~~ of $CaCO_3$ is recycled and reused in the reaction tank.